

THE INTENSITY OF INFRARED ABSORPTION BANDS

A DISSERTATION

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN THE
UNIVERSITY OF MICHIGAN

BY

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An experimental method of measuring the absolute intensities of infrared absorption bands in gases has been used in which the absorbed energy was measured directly by the volume change in the absorbing gas due to the heat evolution in it. The absorption cell was traversed by radiation from a specially constructed infrared monochromator arranged for evacuation. The incident energy density was found through a calibrated thermocouple and galvanometer and the optical characteristics of the monochromator. Measurements were made with various path-lengths of absorbing gas. The absorption was extrapolated to zero by using a logarithmic graph which has many advantages. Line-width forms were investigated. It was found that for CO, $\alpha = \int \alpha_\nu d\nu$ was 1.18×10^{13} for the fundamental vibration band at 4.66μ and 1.54×10^{11} for the harmonic. The corresponding Einstein coefficients and the amplitudes of electric moment were calculated. The results of the analysis show that the Lorentz collision broadening type of line shape satisfies the experimental data much better than other line shapes. The line widths of the fundamental and harmonic bands were observed as 0.10 and 0.12 cm^{-1} at atmospheric pressure which would arise from collision diameters of 5.5Å and 6.1Å respectively. These line widths are smaller than have been previously reported for infrared lines.

IN THE study of spectroscopy two measurables are encountered, frequency and intensity. The qualitative part of the intensity variation with frequency, that is the position of spectral lines has been much more thoroughly investigated than the quantitative, partly because of its greater ease of accurate measurement and partly because the theory concerning line frequencies has been more completely developed and has proved very fruitful. Only a relatively small amount of work has been done on the determination of intensities in spectra. The present article describes the measurement of the absolute intensity of infrared absorption lines.

In the study of the infrared absorption spectra of gases, methods must be used which complicate the calculation of intensities and the only work which can lay claim to accuracy is that of Bourgin¹ and of Dunham² on the intensities of the HCl lines. This article describes the application of an unusual method for the measurement of intensity in the infrared, that of the measurement of the heat evolved in the gas itself during the absorption.

The intensity of absorption in a spectral region is defined as:

$$\alpha = \int \alpha_\nu d\nu \quad (1)$$

where α_ν is the absorption coefficient at frequency ν , that is, the coefficient of the path-length in the expression

¹ Bourgin, *Phys. Rev.* **29**, 694 (1927).

² Dunham, *Phys. Rev.* **34**, 438 (1929).

$$I_x = I_0 e^{-\alpha x} \quad (2)$$

which gives the intensity after the radiation of frequency ν has traversed a path-length x of absorber. This α is related to the Einstein coefficients of the transition causing the absorption by the relations:³

$$\alpha_{ij} = h\nu N B_{ij}/c \quad (3)$$

$$\alpha_{ij} = c^2 A_{ij}/8\pi\nu^2 \quad (4)$$

where the subscripts denote the states involved in the transition, and thence to the matrix component of the amplitude of the electric moment associated with the transition.

$$\alpha_{ij} = 2\pi^3 N^{\nu} (p_{ji})^2 / 3hc. \quad (5)$$

Because of the exponential character of the absorption, of inability to work in the infrared with slit-widths less than the line-width and of ignorance of the line-shape, one cannot find the intensity from measurements of the absorption at a single path-length.² It is, rather, necessary to take readings at several path-lengths x and then extrapolate to $x=0$. To extrapolate with any degree of accuracy sufficiently small values of x must be used. In practice this means the greatest value of α_{ν} must be less than $\frac{1}{2}$. Since the line-width in the infrared, of the order of 0.2 cm^{-1} , is much smaller than the slit-widths used (about 2.0 cm^{-1}), the absorbed energy is only about 1/20th the incident. In the usual type of absorption measurement the incident and the transmitted radiation are measured and from these the absorbed radiation is calculated. The absorption is thus the difference between two much larger quantities, a small error in either of which causes a relatively large error in the result and hence in the determination of intensity.

The present method is an attempt to decrease the large cause of error mentioned above by measuring the absorbed energy directly. This absorbed energy is determined by a micromanometer which measures the volume change in the absorbing gas due to its temperature increase. The incident energy is obtained in absolute measure by means of a calibrated thermocouple. The method suffers from the disadvantage that the absorbed and incident energy must be measured by different means. Many measured quantities enter multiplicatively into the result and thus errors of standardization as well as errors of measurement may exist. In the usual type of absorption measurement the dimensionless absorption is given immediately by the ratio of two galvanometer deflections and no other quantities enter except the path-length. The method employed here does however possess great sensitivity and we believe that the results obtained by it are fully as reliable as those obtained by the usual procedure.

The heat energy liberated in the gas can be taken as a measure of the absorbed energy, since very little energy is reradiated. The mean life of an unperturbed molecule in the vibrational state to which it is lifted by the absorption of infrared radiation is about 10^{-2} secs. Under experimental

³ Tolman, "Statistical Mechanics," (1927 Ed.) p. 175.

conditions used here the molecule suffers 10^8 collisions during this time and it is quite certain that its vibrational energy will become rotational or translational through impact rather than be re-emitted as scattered radiation. The number of molecules having a translational energy greater than $h\nu$ for the fundamental band is about 10^{-4} of the total number of molecules at room temperature.

Gerlach⁴ has investigated this point experimentally in the case of CO_2 and was unable to detect scattered radiation when CO_2 at atmospheric pressure was absorbing infrared. An approximate wave-mechanical solution has been carried through by Zener⁵ in which it is found that the probability of a 1-0 vibration transition of an N_2 molecule due to a head-on collision with an He atom is 6×10^{-8} at room temperature. The fact that this calculated probability is so small does cast some doubt on the assumption which underlies the present work, namely that only a small portion of the radiation escapes measurement by re-emission. The final results may thus be said to form only a lower limit to the value of α . However the large value of α found for CO seems to indicate with considerable definiteness that in this case practically all of the absorbed radiation does become heat and thus also that the vibrational state of the molecule is changed by less than 10^8 collisions.

The absorbed energy ΔE is given by:

$$\Delta E = \int J_\nu (1 - e^{-\alpha \nu x}) d\nu \quad (6)$$

where J_ν is the incident energy stream density lying between the frequencies ν and $\nu + d\nu$. If J_ν is constant over the absorption region and we expand the exponential:

$$\Delta E = J_\nu \int [x\alpha_\nu d\nu + \frac{1}{2}x^2(\alpha_\nu)^2 d\nu + \frac{1}{3}x^3(\alpha_\nu)^3 d\nu \dots] \quad (7)$$

or

$$\lim_{x \rightarrow 0} \Delta E / x J_\nu = \alpha. \quad (8)$$

Experimental measurements were taken for various values of x and the results extrapolated to $x = 0$.

THE MEASUREMENT OF THE ABSORBED ENERGY

The absorption cell and its accessories are shown in Figs. 1 and 2. The monochromator B with the exit slit s_2 and the rocksalt window w_2 furnished the incident beam J . This passed through the absorption cell A via the salt windows and the remaining portion was absorbed by the receiver F . In good thermal contact with A was an almost identical compensating chamber C .

⁴ Gerlach, Ann. d. Physik 5, 4-5, 371 (1930). Some deductions of interest here from the work of Kneser, (Phys. Zeits. 32, 179, 1931) on ultrasonic wave velocity in gases have been published recently by Heil (Zeits. f. Physik 74, 31, 1932). In the case of CO_2 the oscillation corresponding to the 14.9μ band is affected by approximately 10^{-6} of the molecular collisions.

⁵ Zener, Phys. Rev. 37, 556 (1931).

The two chambers were well insulated from external thermal effects and between them the micromanometer was connected so that it might be relatively unaffected by external temperature and pressure fluctuations.

The volume change ΔV due to the radiation was limited by the thermal conductivity of the gas in the absorption cell. With the size of cell used, a

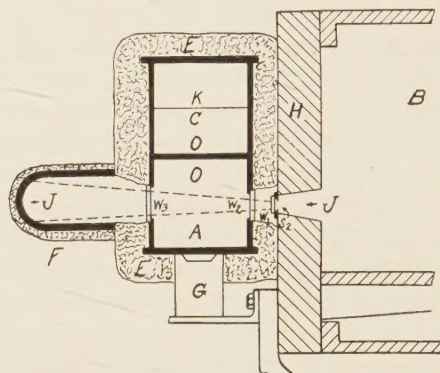


Fig. 1. Lateral section of absorption cell.

10 cm cube, the change in volume was 85 percent completed in 30 secs. after the heat source conditions in the gas were changed; a result which agrees with calculations based on the Fourier theory of heat conduction.

The connection between ΔE and the micromanometer indication can be approximately calculated, but to supplement this calculation a Pt wire 5.65×10^{-3} cm in diameter was placed in the compensating chamber in the position corresponding to that of the beam in the other chamber. The micromanometer was then calibrated by developing a known ΔE in the wire electrically. It can be shown that the line source of the wire and the volume distribution of the beam differ only slightly in their effect on $\Delta E/\Delta V$. Difference in end effect and heat conduction along the wire may also be neglected. No

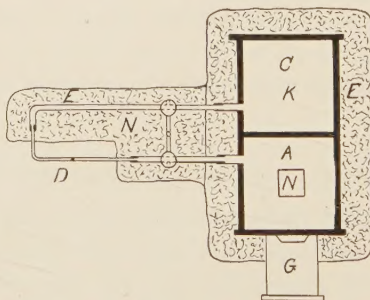


Fig. 2. Front view of absorption cell and micromanometer.

change was found in the resistance of the wire over the range of the currents used. A specially calibrated milliammeter was used to determine the current in absolute measure.

Convection appeared to play no role in the range of extrapolation. Heat transfer by it is proportional to the square of the temperature differences

involved and an approximate calculation showed that the ratio of convected to conducted energy was much less than 2 percent at a value of ΔV equal to 10 times the usable sensitivity of the micromanometer, at which point the measurements had the greatest bearing on the final results. Also no decrease of $\Delta V/\Delta E$ with increase of ΔE which would result from convection was observed within the range of measurements.

The micromanometer consisted of an oil drop in a capillary tube as shown at D in Fig. 2. The drop motion was measured on the eyepiece scale of a telemicroscope focussed on the meniscus. The drop consisted of a higher boiling fraction of kerosene which had sufficiently low vapor pressure and vapor diffusion so that its infrared absorption in the cell was not noticeable. It possessed a viscosity which was sufficiently small so that its position indicated the value of ΔV with no appreciable lag. The sensitivity was $dV=10^{-5}$ cm³; $dp=3\times 10^{-2}$ dynes/cm²; $dT=10^{-5}$ °C. and $dE=1.0$ erg per second developed in the cell which corresponded to a linear movement of the drop of 5×10^{-4} cm.

Capillary forces acting on the drop were about 10^3 times the gas forces to be measured so slight inhomogeneities in the surface of the tube or drop might disturb the readings considerably. Even after thorough cleaning of specially chosen capillary tubing the readings showed small variations which could be traced to this cause. There was also a type of hysteresis in the motion of the drop which was unfortunately most noticeable at small deflections where the readings were most desired.

Small unsteady drifts of the oil drop occurred due to chemical activity, adsorption or thermal leaks through the insulation surrounding the cell. To eliminate the effect of these as well as the variations mentioned above many readings had to be taken. The radiation was allowed to pass through the cell during alternate 30 sec. intervals and readings taken at each movement of the shutter. The difference between a reading and the mean of its two neighbors was taken as the effect of the radiation. This eliminates the effect of uniform drift and when the mean of such differences was taken, the higher derivatives of drift with respect to time tended to disappear because of their variability. All readings of which records are shown represent such averages.

To eliminate the uncertainty caused by the hysteresis in the oil drop motion, readings were taken for various currents, i , in the compensating wire and a graph plotted between i^2 and " s ," the drop deflection. Both positive and negative s 's were used and the intercept on the $s=0$ axis of the best mean straight line through the points gave the value of i^2 corresponding to the radiation. As an aid in determining these lines, those for various absorbing path lengths were plotted on the same graph. The slopes should be the same, but the intercepts different. Readings could be reproduced to 1 erg per sec.

THE MEASUREMENT OF THE INCIDENT ENERGY

A monochromator as shown in Fig. 3 was constructed to select the required frequency range and to enable the measurement of the energy density

in it. The instrument was designed for use with wide slits to insure the maximum intensity of radiation J_ν but with small enough aberration so that the variation of J_ν with frequency ν of the beam issuing from the monochromator was known with sufficient accuracy. The path of the radiation from the Nernst glower N to the absorption cell A is shown by the dotted line. The mirror was of 50 cm focal length and the rocksalt prism P was of $17\frac{1}{2}^\circ$ angle and had 10×15 cm faces.

All the monochromator parts were mounted on the head H . The cover Q was of heavy iron pipe furnished with a flange R which made a ground joint contact with the corresponding part of H and was mounted on rollers which fitted rails on the base so it could be rolled back from H . The slit widths and the prism table rotation could be controlled by micrometer screws projecting through cones in the head H . The radiation could be interrupted by a magnetically operated shutter t . The exit slit was covered with an NaCl window. The monochromator could be evacuated to 10^{-2} mm Hg pressure and thus the greater part of the H_2O and CO_2 removed from the path. This was not necessary however in the CO measurements as the CO bands do not overlap those of the above named gases.

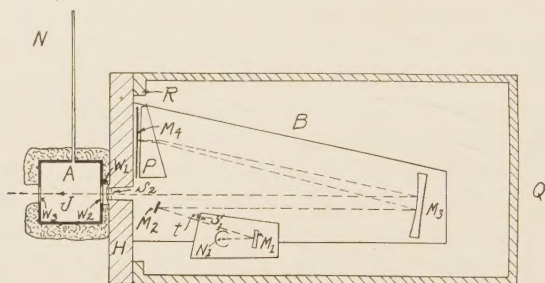


Fig. 3. Top view of monochromator.

The Nernst glower was preheated to start it, the monochromator sealed, evacuated and refilled with air drawn through a liquid air trap. The glower could be kept heated at a low temperature for long periods without deterioration. During readings the current could be kept constant to within 1 percent by manual adjustment. To decrease the effect of plastic movement of the glower its focus on the incident slit was made broad.

The monochromator was focussed by the use of the Na D lines. The breadth of focus due to aberration was 0.2 mm or 0.2μ at 3.0μ . The wavelength calibration of the micrometer controlling the prism rotation was accomplished by the use of the dispersion curve of NaCl and the micrometer readings for the Na D lines. This calibration predicted the position of the various absorptions. The dispersion was also used to calculate the slit widths in frequency units, a magnitude which enters directly into the final results. The slit widths in cms were measured with the micrometer screws which adjusted them externally, the calibration being checked with a microscope.

The above optical facts concerning the monochromator allowed the calculation of the shape and the position of the energy distribution curve shown

idealized in Fig. 4. In constructing this figure it has been assumed that the monochromator possessed an ideal focus, that the incident slit was uniformly illuminated and that I_ν , the radiation of the source per unit frequency interval, was a constant. The width of the wings g equals the frequency width of the narrower slit $\Delta\nu_2$ and h the width of the region of maximum J_ν equals $|\Delta\nu_1 - \Delta\nu_2|$.

$J = \int J_\nu d\nu$, the total radiation issuing from the monochromator was found by removing the absorption cell and focussing the exit radiation on a thermopile with a mirror. The thermopile and mirror combination was calibrated in absolute measure by illuminating the exit slit s_2 with a standard incandescent lamp from the Bureau of Standards. This allowed the thermopile calibration in situ with the same radiation distribution over the thermopile surface as in the actual measurements. Correction was made for the NaCl windows traversed.

From Fig. 4

$$J = \int J_\nu d\nu = J_\nu(\text{max.}) \Delta\nu(\text{max.})$$

or

$$J_\nu(\text{max.}) = J / \Delta\nu(\text{max.}) \quad (9)$$

where $\Delta\nu(\text{max.})$ is the frequency width of the widest slit and $J_\nu(\text{max.})$ is the greatest value of J_ν in Fig. 4.

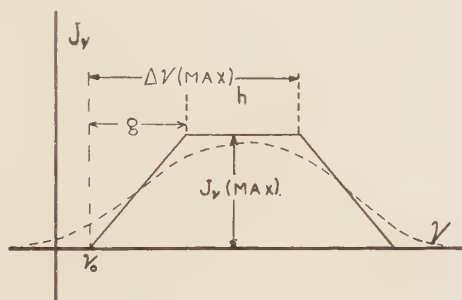


Fig. 4. Incident energy versus frequency.

Eq. (9) was used to calculate $J_\nu(\text{max.})$ which is that operating on the absorbing gas. It was found that the variation of illumination density over the incident slit and the variation of I_ν with ν which would disturb the validity of (9) could be neglected. It should be noted here that it is I_ν which is considered rather than I_λ which would vary considerably with ν or λ . I_ν and J_ν are used because it is an α_ν and an $\int \alpha_\nu d\nu$ which is discussed. The correction for the effect of aberration and nonidealness of focussing will be noted later.

In some cases; i.e., that of CO, the band whose intensity is desired lies close to, but still does not overlap, an absorption band of the atmosphere. J_ν at the position of absorption is not changed, but (9) is not valid, since part of the area under Fig. 4 is removed. To enable results to be taken at

any ν a curve was made of J versus prism rotation and the regions of absorption bridged by interpolation.

THE MEASUREMENT OF $\Delta E/xJ_\nu$

The factor in (8) not yet treated is x , the effective path length of the absorbing gas. This was measured in units of cms at 76 cm Hg pressure and 300°K. The cell was evacuated with a Hyvac and Hg vapor pump and filled with the partial pressure of absorber giving the desired path length. The absorber was then diluted to atmospheric pressure with air which had been drawn through sodium hydroxide solution, sulfuric acid and a liquid air trap. This treatment decreases to negligible concentration all the polar constituents of air except CO.

The CO used was made by dropping formic acid on sulfuric and was drawn through sodium hydroxide solution, sulfuric acid and finally liquified with liquid air. The middle boiling fraction of this liquid was used. All sur-

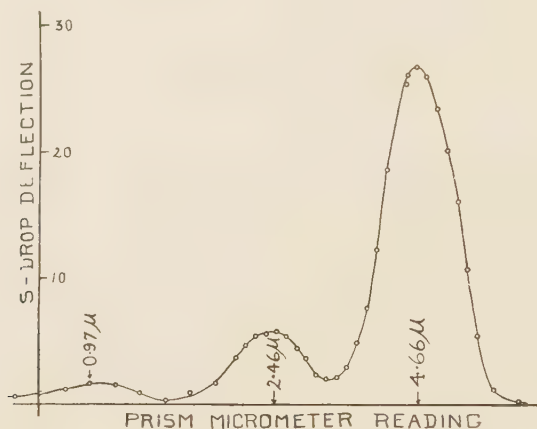


Fig. 5. Absorption versus incident wave-length.

faces in contact with the gas were of glass except for short lengths of protected rubber tubing and the inside surface of the copper absorption cell which was coated with ceresin. During a set of measurements x was halved after each reading and thus small x 's reached with accuracy. The gases were removed by pumping and flushing the cell with air freed from CO_2 and H_2O . A small residual drop deflection remained which had to be corrected for. It was apparently due to absorption and scattering of the beam by the windows.

In beginning the study of any gas the slits were adjusted to resolve bands 1μ apart, the cell filled with the gas and an absorption spectrum of drop deflections plotted against prism rotation as shown in Fig. 5 for CO. The fundamental at 4.66μ and the harmonic at 2.35μ are present. The slight maximum at 1.0μ could not be explained and seemed to disappear with decrease in x of CO.

It is seen that the peak of the absorption curve is not flat, as Fig. 4 would lead one to believe it should be. Most of the width of this curve is due to the width of the absorption band itself, but part comes from the non-idealness

of the incident energy curve illustrated by the dotted line shown in Fig. 4. The correction for this non-idealness was found by increasing $\Delta\nu(\text{max.})$ or the greater slit width and finding how the maximum absorption as indicated in Fig. 5 increased. As s_2 is made large with respect to the aberrations $J_\nu(\text{max.})$ approaches its ideal value. Curves, such as Fig. 5, were plotted for several values of $\Delta\nu(\text{max.})$. It was found that about 10 percent should be added to the maximum s 's obtained when using $\frac{1}{2}$ and 1 mm slits in order that they represent the s 's due to the J_ν calculated from Eq. (8).

When the absorption regions were located their wave-lengths were checked. Readings were then taken at the maxima in Fig. 5 for a series of x 's. Thus as experimental data one possesses a series of i^2 's corresponding to various x 's. The most accurate method of obtaining α from these will be discussed in the next section.

THE THEORETICAL DERIVATION OF $\Delta E/xJ_\nu$

It is possible to calculate the variation of ΔE with x from α and the line width if one assumes a line shape and the relative intensity of the lines in a band. We shall indicate the results for a band, such as that of CO, with no zero branch. The line shape shall be assumed to have the form:

$$\alpha_{\nu j} = r_j b^2 / [b^2 + (\nu - \nu_j)^2]. \quad (10)$$

Where r_j is the height or absorption coefficient at the peak of the line j , b is defined as the line width and ν_j is the center of the line. It is seen that b is the distance from ν_j to where $\alpha_{\nu j}$ has fallen to $\frac{1}{2}$ its value at ν_j .

$\Delta E_j = J_\nu \int (1 - e^{-\alpha_{\nu j} x}) d\nu$, where J_ν is treated as a constant.

$$= J_\nu \sum_{n=1}^{\infty} \frac{(-1)^{n-1}}{n!} \int (\alpha_{\nu j})^n d\nu. \quad (11)$$

Using (10) and considering only one line, we may integrate each term:

$$\Delta E_j = \pi b \sum_{n=1}^{\infty} d_n (lr_j)^n \quad (12)$$

where

$$d_n = \frac{(-1)^{n+1} (2n-3)(2n-5) \cdots 1}{n!(n-1)! 2^{n-1}}.$$

The results may also be expressed in Bessel functions,⁶ but this form was not found as apt for the purpose as the above.

THE ENERGY ABSORBED BY A BAND BRANCH

Let us consider the ΔE due to one branch of a band, taking b the same for all the lines and letting the relative intensities of the lines be given by:

$$r_j = c j e^{-\sigma j^2}$$

where $\sigma = h^2 / 8\pi^2 I k T$. This arises from the application of old quantum theory but is sufficiently correct for the present purpose. Let $\sum_{j=1}^{\infty} r_j = R$. Then, if

⁶ Ladenburg and Reiche, Ann. d. Physik **42**, 181 (1913).

we replace the summation by an integration which is allowable here, we find:

$$r_j = 2R\sigma j e^{-\sigma j^2}. \quad (13)$$

Substituting (13) in (10) we find:

$$\frac{\Delta E}{J_\nu} = \sum_{n=1}^{\infty} \frac{(-1)^{n+1}}{n!} x^n \int \left[\sum_{j=1}^{\infty} \frac{r_j b^2 d\nu}{b^2 + (\nu - \nu_j)^2} \right]^n.$$

We may now approximate

$$\left[\sum_{j=1}^{\infty} \alpha_{\nu j} \right]^n \quad \text{by} \quad \sum_{j=1}^{\infty} (\alpha_{\nu j})^n$$

This neglect of the cross product terms in the expansion is equivalent to neglecting the effect of line overlapping. In the case of CO it may be shown that the cross product terms may be neglected to $n=10$ and $xr_j(\text{max.})=4.0$. This allows evaluation of the series for large enough values of x to overlap the region of experimental data in which the accuracy decreases with decreasing x .

We may now integrate with respect to ν after interchanging $\int d\nu$ with $\sum_j$.

$$\frac{\Delta E}{J_\nu} = \sum_{n=1}^{\infty} \pi b \frac{(-1)^{n+1}}{n!} \frac{(2n-3)(2n-5) \cdots 1}{(n-1)! 2^{n-1}} \sum_{j=1}^{\infty} x^n \nu_j^n. \quad (15)$$

Substituting the value of r_j from (13) we may replace $\sum_j$ by $\int dj$ with an error less than 2 percent for each term, when n is less than 10. The integration with respect to j may now be carried out and gives:

$$\Delta E/J_\nu = \sum_{n=1}^{\infty} g_n x^n. \quad (16)$$

We must find the effect of this heat when it is liberated along the length of the beam in the absorption cell. The cube of 10 cm on an edge has a difficult heat conduction solution where sources are concerned, but the present situation can be approximated by a sphere of about 5 radius with the beam traversing a diameter.

Consider a sphere of radius a with its surface temperature constant which is filled with a gas of heat conductivity ρ . A heat source of strength ϵ at a distance b from its center causes a change in temperature ΔT which may be calculated at any point by image theory. The volume change due to this ΔT throughout the gas is then:

$$\Delta v = \int \Delta T dv / T \quad (17)$$

$$= \epsilon(a^2 - b^2)/6\rho T. \quad (18)$$

To find the effect due to the heat absorption taking place in the length of the beam, we introduce a coordinate q measured along the length of the

beam from its incident end; then (18) becomes:

$$\Delta v = \epsilon(2aq - q^2)/6\rho T. \quad (19)$$

The ΔE in (16) occurs over a length $2a$, i.e., the total beam length in the cell. For the absorption in any length q with an effective path length x in the cell we need merely substitute $qx/2a$ in (16) for x . Thus the heat absorbed between q and dq is:

$$\begin{aligned} \epsilon(q) &= \frac{\partial \Delta E(q)}{\partial q} \\ &= g_n \left(\frac{x}{2a} \right)^n n q^{n-1} \end{aligned} \quad (20)$$

Substituting (20) in (19) and integrating with respect to q

$$\Delta v = \frac{\pi b a^2}{18\rho T} \sum_{n=1}^{\infty} h_n U^n. \quad (21)$$

Where $U = 2Rx(\sigma)^{1/2}$ which corresponds to a mean absorption line height and

$$h_n = \frac{3(2n-3)(2n-5) \cdots 1[(n-1)/2]!}{(n+2)!(n-1)!n^{(n-1)/2}2^{n-2}} \text{ for } n \text{ odd}$$

and

$$h_n = \frac{3\pi^{1/2}(2n-3)(2n-5) \cdots 1.3.5 \cdots (n-1)}{2^{(3n-4)/2}(n+2)!(n-1)!n^{(n-1)/2}} \text{ for } n \text{ even.}$$

The numerical values of h_n were calculated for values of n to 10. The value of $g = \sum_{n=1}^{10} h_n U^{n-1}$ was calculated for values of U ranging from 0.1 to 10 and was plotted versus U . This graph corresponds to the experimental graph of i^2/x versus x where i^2/x is proportional to the energy absorption per molecule.

The slope of this curve at the origin is definitely related to the line width b . One can deduce the connection from (21).

$$\begin{aligned} \left[\frac{x}{i^2} \frac{d}{dx} \left(\frac{i^2}{x} \right) \right]_{x=0} &= \frac{\alpha}{16b} \left(\frac{\sigma}{2\pi} \right)^{1/2} \\ \text{or } b &= \frac{\alpha}{16} \left(\frac{\sigma}{2\pi} \right)^{1/2} x_1 \end{aligned} \quad (22)$$

where x_1 is the value of x at the intersection of the $i^2/x=0$ line and the tangent to the i^2/x line at $x=0$.

The experimentally determined values of i^2/x were plotted versus x , the graph being modeled after that of $g = h_n U^{n-1}$ versus U . The results for one set of readings are shown in Fig. 6.

It was found that for large values of x the absorption was quite accurately equal to a power of x . This immediately suggested plotting the data on logarithmic scales. Fig. 7 shows the resulting theoretical curve, and Fig. 8,

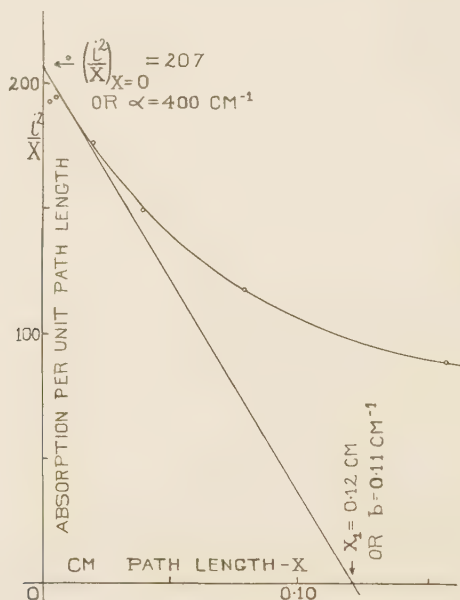


Fig. 6.

the experimental points with the best fitting theoretical curve superposed, determined by mere movement of Fig. 7 over the points of Fig. 8. It is seen that, for the larger values of x , the experimental curve is a straight line; i.e.,

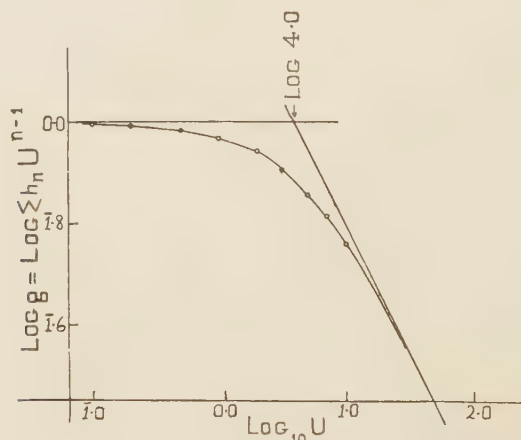


Fig. 7.

i^2/x is proportional to x^n where n is approximately equal to $-\frac{1}{2}$. The theoretical curve is provided with a like asymptote whose presence is justified on the grounds that all experimental curves taken for the CO fundamental had such

a behaviour for path lengths x greater than 1.0 mm and that the theoretical curve for a single line in the band given by Eqs. (11) and (12) has such a behaviour.⁷

With this type of plotting, the determination of α reduces to finding the position of the horizontal asymptote to the experimental curve at low values of x . The value of i^2/x of this line is that where the absorption is proportional to the number of atoms present and is proportional to α .

A comparison of Figs. 7 and 8 allows the scale factor in the abscissae; i.e., the ratio between U and x , to be found. As a reference point the intersection of the two asymptotes of each curve was used. The definition of U ; i.e.,

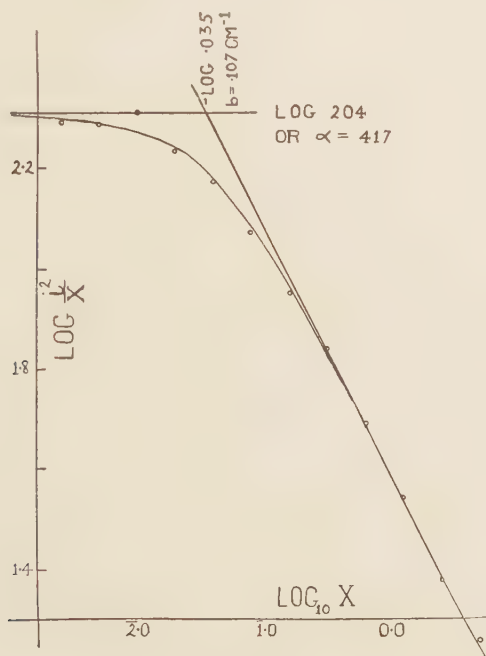


Fig. 8.

$U = 2R(\sigma)^{1/2}x$, allowed the calculation of R . b was then calculated from $\alpha = 2\pi Rb$. The value of b obtained in this way agrees numerically with that calculated from Eq. (22) applied to a different type of graph, i.e., Fig. 6.

It is seen that to determine α or the position of the horizontal asymptote, small enough x must be used so that x is not in the region where ΔE is proportional to $(x)^{1/2}$ but in the region where ΔE is at least beginning to be proportional to x . Not only must measurements be taken at several x 's in any absorption measurement, but one must take some of them at a sufficiently small value of x , which is, as seen from Fig. (8), less than 1.0 mm of CO for the fundamental absorption band. This is smaller than has usually been employed heretofore in infrared absorption measurements. Results obtained with greater path length merely define a lower limit for α , since they determine a

⁷ The asymptotic expansion of Eqs. (11) and (12) is proportional to $x^{1/2}$ for large x 's.

lower limit for the position of the horizontal asymptote as can be seen immediately from Fig. 8. This result which is an important one applies also to measurements made on a single line. It appears that a rediscussion of some of the earlier experimental work on infrared intensities might be desirable.

The value of $\log \Delta E/xJ_\gamma$ from (11), that is for a single line, was plotted versus $\log x$. The experimental values of $\log (\text{absorption}/x)$ from several lines in the HCl absorption band at 3.5μ as determined by Bourgin¹ were plotted versus $\log x$ also. It was found that lower values of r were used in the present method than had been used by Bourgin; that is, the sensitivity of this method is greater. This does not however imply that the measurements based upon the older methods might not be improved as regards sensitivity. Recent developments in the field of amplification of thermoelectric currents would allow the use of narrower slits at shorter path lengths, thus permitting greater accuracy to be attained. Also there are a greater number of measurements with their possibilities of accompanying errors in the present method.

A set of data is shown below embodying the mean of the various determinations. The value of $\sigma = h^2/8\pi^2 I k T$ used was 0.0088 corresponding to a value⁸ of $I = 1.50 \times 10^{-39}$ and a temperature of 300°K .

TABLE I.

	Fundamental, ($n = 1$) at $4.66\mu = 2150 \text{ cm}^{-1}$	Harmonic, ($n = 2$) at $2.35\mu = 4260 \text{ cm}^{-1}$
$J = \int J_\nu d\nu$ through slit	$7.79 \times 10^3 \text{ ergs/sec}$	$4.24 \times 10^4 \text{ ergs/sec}$
$\Delta\nu$ included in 1.0 mm slit	440 cm^{-1}	2200 cm^{-1}
$J_\nu(\text{max.})$ corrected	$14.7 \text{ ergs/sec. cm}^{-1}$	15.9
$\lim_{x \rightarrow 0} \frac{i^2 - (i^2)_0}{x} (i \text{ in m.a.})$	204	2.87
$\alpha_{on} = \lim_{x \rightarrow 0} \frac{\Delta E}{x J_\nu}$ $= \frac{R}{J_\nu} \lim_{x \rightarrow 0} \frac{i^2 - (i^2)_0}{x}$	$394 \text{ cm}^{-1} = 1.182 \times 10^{13}$	$5.13 \text{ cm}^{-1} = 1.54 \times 10^{11}$
B_{on} from Eq. (3)	3.40×10^{16}	2.23×10^{14}
A_{no} from Eq. (4)	55.7	2.85
$\tau_{no} = \frac{1}{A_{no}}$	0.0180 secs.	
p_{no} from Eq. (5)	2.65×10^{-19}	2.15×10^{-20}
ϵ_{no}	$3.9 \times 10^{-10} \text{ e.s.u.}$	
R_{no}	610	9.8
$b_{no} = \alpha_{no}/2\pi R_{no}$	0.103 cm^{-1}	0.125 cm^{-1}
d_{no}	5.5A	6.1A

One may calculate an effective electric charge ϵ which, if it were concentrated on the nuclei and moved with them, would give the observed intensi-

⁸ Snow and Rideal, Proc. Roy. Soc. A125, 462 (1929).

ties of absorption and emission from the formula:⁹

$$\alpha = \frac{\pi N \epsilon^2}{3c\mu} \quad (24)$$

Eq. (24) gives a value of $\epsilon_{01} = 3.92 \times 10^{-10}$ e.s.u. = 0.82 e . This is quite large compared to the permanent effective charge of 0.022 e calculated from the internuclear distance and from the permanent dipole moment obtained from dielectric constant measurements.¹⁰ There is however no reason to suppose that any simple relation exists between these two effective charges.

An accurate wave mechanical analysis of the intensities in terms of the electric moment and its derivatives and the anharmonicities in the mechanical motions of the nuclei has been carried out by Dunham.¹¹ The values of α_{01} and α_{02} obtained above and the coefficients in the power series expansion of potential energy versus nuclear separation found for CO⁸ were used in Eq. (9) of Dunham's article. The values of the first and second derivatives of the electric moment with respect to the nuclear separation were calculated assuming Dunham's a_3 and p''' equal to zero.

The results found were

$$\begin{aligned} p' &= \pm 9.1 \times 10^{-18} \text{ e.s.u.} \\ p'' &= \mp 3.4 \times 10^{-18} \text{ e.s.u.} \\ &\text{or } \pm 3.7 \times 10^{-18} \text{ e.s.u.} \end{aligned}$$

where the +3.7 and the -3.4 are to be taken with the positive value of p' . The derivatives appear large with respect to the equilibrium electric moment, $p = 0.118 \times 10^{-18}$ e.s.u.

In the method used no large error is expected in the derivation of R , since it does not depend on standardized measurements, but only upon x and relative i 's. The probable errors in the various measurements were estimated and with liberal allowances the probable error in the result was about 30 percent. It is believed that the results are correct to within that order of magnitude at least.

The fact that at large values of x the absorption was proportional to $(x)^{1/2}$ leads definitely to a line shape of the form of Eq. (9). Other line shapes, for instance the error curve, not having the same behavior at large distances from the line center are definitely eliminated. Working over a smaller range of x 's others have found that Eq. (9) gives a somewhat better representation of the absorption than other line shapes do. Curves such as Fig. 8 taken during this work furnish much more definite proof of this.

Classically this line shape arises from the Lorentz theory of collision broadening. During a collision the motion of the radiating body is changed in frequency or in phase, resulting in an effective chopping off of the monochromatic wave train being emitted or absorbed. The classical treatment

⁹ Dennison, Phys. Rev. **31**, 510 (1928).

¹⁰ Zahn and Miles, Phys. Rev. **32**, 497 (1928).

¹¹ Dunham, Phys. Rev. **35**, 1347 (1930).

of the effect on the absorption line of such an interruption assuming a definite cross-section of the molecules for collision, but allowing a distribution of velocities and mean free paths, has been worked out by Dennison.⁹ He has shown that the resulting line shape is very closely given by a formula of the type (10) where the half width b can be related to σ the collision diameter, $\bar{v}$ the mean square velocity and N the number of molecules per cc. The actual formula is

$$b = n\sigma^2 \left(\frac{7.60 kT}{2\pi m} \right)^{1/2} = 0.78 n\sigma^2 \bar{v}. \quad (25)$$

The results of the application of Eq. (25) to the experimentally determined values of b are to be found in Table I. The values of σ found are somewhat larger than that calculated from gas kinetic data which is about 4.5Å. However the magnitudes being measured in the two cases are not identical since a collision which is effective in determining the line shape may alter only the phase of a rotating molecule without affecting its energy. It should be emphasized that the line width is not an intrinsic property of the molecules as is intensity. The line width is determined by the type and frequency of the collisions. Also it might possibly be quite different for a CO molecule in an atmosphere of CO than in an atmosphere of N₂ even though the gas kinetic phenomena would be almost the same.

It is probable that most of the collision perturbation arises through its effect on the molecular rotation. The vibration is little affected by thermal collisions, while it appears that the rotational state is changed at about every gas kinetic collection.^{5,12} However the collision diameter considered in these references need not be the same as that calculated here. A change of phase can affect a wave train but not an energy except in its uncertainty. It would seem that phase change may be a measurable quantity in line width determinations.

In conclusion it may be said that a method of measuring infrared absorption intensities has been tried and found satisfactory although somewhat cumbersome. It suffers from the fact that many absolute measurements must be made in which errors of standardization may easily arise. The final accuracy, while not large, appears to be definitely better than that previously attained owing to a greater sensitivity of the apparatus.

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¹² Oldenberg, Phys. Rev. **37**, 194 (1931).

